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## THE CHEMICAL STATUS OF ZINC IN THE SOIL WITH METHODS OF ANALYSIS<sup>1</sup>

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### CONTENTS

	PAGE		PAGE
Introduction .....	1	Solvents for extracting available zinc.....	12
The soils studied.....	3	Estimation of total zinc in soil.....	22
Analytical methods .....	4	Effect of removal of organic matter.....	22
Purification of apparatus and chemicals...	5	The status of zinc in the soil.....	23
Methods of separating extracts from		Summary .....	27
undissolved matter .....	7	Literature cited .....	29

### INTRODUCTION

ZINC has long been known to occur in the soil in minute amounts, but little is known about the forms in which it occurs and the extent to which it occurs in forms available to plants. Rather recently, zinc deficiencies have been shown to be a cause of certain disorders of plants. In California an elaborate, systematic investigation has been made of the relation of zinc to little-leaf of deciduous fruit trees and to mottle-leaf of citrus trees; the history of this investigation and a review of literature on the subject is given by Chandler (6).<sup>4</sup> These discoveries have emphasized the need for a laboratory test for available zinc in soils.

Twenty or thirty years ago, a few European workers reported studies on zinc naturally present in soils and on its importance as a plant nutrient. Although some references to the effect on soils of added zinc salts had previously been made by several investigators (6), it was not until 1936, in the United States, that extensive studies of soils as a source

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<sup>4</sup> Italic numbers in parentheses refer to "Literature Cited" at the end of this paper.

of zinc for plants were reported by Jones, Gall, and Barnette (10) and Barnette *et al.* (3) in Florida, and by Alben and Boggs (1) in Louisiana and Texas. Barnette *et al.* found that fallowing the soil improved the growth of corn on soil deficient in power to supply zinc to plants, and that addition of superphosphate along with the zinc rendered the zinc less effective in curing white bud of corn. In 1934, Alben had stated that pecan rosette was much less severe on slightly acid than on somewhat alkaline soils.<sup>5</sup> More recently, Alben and Boggs (1) gave the results of their study of numerous soils in relation to pecan rosette, indicating that more rosetting occurs on soils moderately alkaline and that the total zinc content of these alkaline soils is frequently higher than that of the more acid soils. Jones, Gall, and Barnette (10) reported a study of the effects on soils of added zinc salts, and stated that zinc exists in soils in three conditions—water-soluble, exchangeable, and relatively insoluble, namely, that which is present as phosphate, carbonate, silicate, or other difficultly soluble compounds. Boggs and Alben (4) in 1936 described a procedure for estimating the zinc in soils and gave some results.

In 1937 a dithizone method for determining zinc solution was reported (8). This method is sufficiently sensitive and rapid but lacks selectivity: some fifteen or twenty metals under widely varying conditions respond to this test. Of these, zinc, copper, lead, cobalt, nickel, and manganese are found in soil in small amounts. Fairly reliable separations were worked out in 1938 (9) so that small amounts of zinc, copper, cobalt, and lead may be determined with sufficient precision and without too great expenditure of time.

There remained the problems of extracting from the soil the minute amounts of zinc it contains and of separating the extract from the insoluble matter of the soil. Of chief interest, of course, is the estimate of the amount of zinc naturally available<sup>6</sup> to plants. The main purpose of this investigation, therefore, has been to discover a satisfactory method for extracting available, as distinguished from total, zinc. The search for this method has been long and laborious and is at present only partly successful. The adopted procedures have been worked out by trial-and-error routes; to enable others to avoid repeating unsuccessful experiments, a rather full account of the various procedures attempted is given. Some phases of the investigation concerned the forms in which zinc occurs; but the need of plants for zinc was not studied, and this paper treats of it only incidentally.

<sup>5</sup> Alben, A. O. Personal communication, Sept. 15, 1934.

<sup>6</sup> In this paper, the word *available* is employed to mean that which is easily soluble and presumably may be readily taken up by plant roots.

## THE SOILS STUDIED

Some twenty-five soils of diverse character and from several localities, mostly in California, have been studied. With most of them, the behavior of fruit trees on them before and after zinc application was known

TABLE 1

SOILS USED FOR ZINC STUDIES: NAMES, LOCATIONS, pH, AND PRODUCTIVITY

No.	Soil	Location	Depth, inches	pH	Crop conditions
30	Fresno fine sandy loam.....	Fresno	0-12	7.0	Very productive
35	Holland loam.....	Santa Cruz	0-12	6.0	Prune dieback
59	Aiken clay.....	Paradise	0-12	6.2	Deficient in $PO_4$
64	Vina loam.....	Durham	0-12	7.0	Deficient in $PO_4$ and K
65	Yolo loam.....	Santa Clara	0-12	7.0	Very productive
78	Gold Ridge fine sandy loam.	Forestville	0-24	5.3	Little-leaf
80	Hanford fine sandy loam....	Porterville	0-24	8.0	Alkaline
86	Holland loam.....	Santa Cruz	0-12	5.3	Prune dieback
89	Gold Ridge fine sandy loam.	Sebastopol	Surface	5.3	Little-leaf
90	Aiken clay.....	Paradise	Surface	6.1	Deficient in $PO_4$
95	Ramona loam.....	Riverside	6-24	8.3	Fairly good
103	Aiken clay.....	Paradise	0-14	5.9	Virgin soil
112	Delhi fine sand.....	Delhi	24-48	7.81	Little-leaf
121A	Adobe.....	Milpitas	6-12	7.7	Apricots in old corral injured
121B	Adobe.....	Milpitas	18-24	7.9	
122	Delhi fine sand.....	Delhi	36-60	7.1	Peach dieback
125	Delhi fine sand.....	Delhi	36-60	7.7	Peach dieback
127B	Not known.....	Concord	36-54	7.4	Corral
129	Delhi coarse sand.....	Delhi	72-84	7.4	Very poor
136A	Delhi sand surface.....	Manteca	Surface	6.7	.....
136B	Delhi sand subsoil.....	Manteca	48-60	8.1	Little-leaf
137	Delhi sand.....	Manteca	24-36	7.1	Little-leaf
138	Delhi fine sand.....	Delhi	36-60	6.9	Little-leaf
144	Pledger clay.....	Arkansas	?	7.1	Pecan rosette
145	Delhi fine sand.....	Delhi	36-60	6.90	Poor

before they were collected, through observations of them in the field by Chandler (6).

The composition and general character of the soils is given in tables 1 and 2.

The samples used were taken from large lots of soil collected by several persons, at various times and places. In collecting and preparing these soils, no precautions were taken to prevent contamination with zinc, so that in some cases the amounts of zinc found may be greater than those normal to the soil. This is not important for the purposes of this investigation—to discover principles and work out appropriate methods. But when soils are to be examined and rated for available zinc, they should be collected in a way to avoid contamination with any metal, particularly zinc.



TABLE 2

MINERAL COMPOSITION OF 1:1 WATER EXTRACT AND PERCENTAGE OF  $\text{CaCO}_3$ , SAND, SILT, AND CLAY IN SOILS

Soil no.	Mineral composition of 1:1 water extract								Per cent of soil			
	Ca	Mg	Na	K	$\text{HCO}_3$	Cl	$\text{SO}_4$	Org.	$\text{CaCO}_3$	Sand	Silt	Clay
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	per cent	per cent	per cent	per cent
30	25	10	?	18	60	10	22	++	0	72	21	7
35	15	4	?	6	20	20	—*	+	0	59	12	29
59	15	4	?	11	15	56	3	+	0	34	18	48
64	11	5	17	2	22	34	5	+	0	40	50	10
65	29	10	10	9	108	15	15	++	0	55	13	32
78	8	4	5	2	7	14	7	tr	0	70	14	16
80	16	4	?	2	80	10	5	+	0.4	55	25	20
86	22	8	5	9	12	20	—	+	0	55	14	31
89	20	8	5	4	tr	18	0	tr	0	82	5	13
90	24	14	2	13	19	12	0	+	0	—	—	—
95	25	33	27	2	50	20	40	tr	tr	64	17	19
112	10	3	13	5	36	10	7	tr	0	87	9	4
121A	27	23	67	45	161	36	149	245	—	—	—	—
121B	32	51	91	49	195	92	154	530	—	—	—	—
122	11	4	14	0.2	27	20	3	—	—	—	—	—
125	14	4	7	0.4	24	12	1	—	—	—	—	—
127B	59	34	158	139	51	72	151	—	—	—	—	—

\* Dashes indicate data not available.

## ANALYTICAL METHODS

The usual standard methods of analysis were used for estimation of the chief constituents of soil.

*Dithizone Method.*—The dithizone method (8) was used for estimation of zinc and some other metals present in very small amounts. On account of its convenience and high sensitivity, this method is very useful and satisfactory. Without it, much of this work would hardly have been possible.

Briefly, the dithizone method is carried out as follows: To the aqueous solution to be tested add a little citrate to prevent precipitation of iron, aluminum, manganese, etc., which otherwise might cause difficulty; then ammonia till slightly alkaline; chloroform; and dithizone solution. Shake the mixture in a separatory funnel. After the liquids separate, draw off the chloroform layer into another separatory funnel and wash with dilute ammonia to remove excess dithizone. The chloroform now contains the dithizone compounds of zinc and of some other metals previously present in the aqueous solution.

*Separating Zinc from Certain Other Metals.*—From the dithizone extract, remove the zinc and lead by shaking with 0.05 N HCl. Then make the acid aqueous solution containing the zinc alkaline again and extract

the zinc by dithizone in chloroform as at first. Copper, cobalt, and perhaps other metals, remain in the chloroform as dithizonates. By suitable adjustment of pH, they may be separated. The amounts of all these metals, after separation, may be estimated by iodometry or sometimes by colorimetry, as described in a previous paper (9).

A small amount of lead also is frequently found. If present, it will be included with the zinc, from which it may be separated by means of KCN as follows: Prepare the solution as usual for the dithizone test, add 1 per cent KCN, and extract with dithizone as usual. Under these conditions, only lead, bismuth, palladium, and thallium react with dithizone. It is assumed that of these only lead is present in the soil extract: the other three metals are not likely to occur in ordinary soils in appreciable amounts. The amount of lead extracted is found by color comparison with a known amount of lead treated in the same manner. The lead thus estimated is to be subtracted from the sum of the zinc and lead found as above outlined.

#### PURIFICATION OF APPARATUS AND CHEMICALS

Ordinary soils contain only extremely small amounts of zinc. Consequently, it is necessary to remove, as far as possible, the small amounts of zinc on or in nearly every piece of apparatus and in the reagents, before they are used for analytical work.

*Apparatus.*—Apparatus is first cleaned by acids in the usual way. This does not always remove the silicious film, which sometimes adheres very firmly to glassware after it has contained soil or soil extracts: the inner surface of a 500-cc separatory funnel that has contained a soil extract in which were 50 gammas of zinc, may retain against washing with water 2–7 gammas of zinc in the silicious film on the glass. Most of this adhering zinc may be dissolved off by a few cc of 0.05 *N* HCl. The remainder is easily removed with dilute HF, which should immediately be washed off with distilled water free of zinc and other metals.

If this zinc in the adhering film is not removed, some of it may go into the acid soil extract next placed in the separatory funnel and thus vitiate the result.

Filter paper or paper pulp is freed of zinc by the same sort of washing. The purification of reagents has been described in previous papers (8, 9) except for special cases, which will be given in connection with the use of the reagents. Metallic apparatus should not contain copper or zinc; preferably it should be of platinum or aluminum. Glass or porcelain ware should not contain zinc; Pyrex glass has been found generally satisfactory.

*Potassium Chloride Solution.*—KCl, used in extracting zinc from soil, is not obtained free of zinc by the modification of Steinberg's procedure (11) employed in this laboratory, namely, heating the solution with  $\text{CaCO}_3$  in the autoclave. The zinc in KCl solution may be brought very low by repeated extraction of the slightly alkaline solution with a chloroform solution of dithizone, but this is tedious.

Since most soils have the ability to fix much zinc, soil was used to extract the zinc from a normal solution of neutral commercial KCl. A liter of the salt solution was shaken for a few hours with 50 grams of a somewhat alkaline clay soil. After settling overnight, the clear solution was found more nearly free of zinc than if prepared by any other procedure: a liter of the solution contained about 3 gammas of zinc, or 0.003 p.p.m.

Later, it was found best to percolate the neutral KCl solution through a mass of soil 3 inches deep in a percolator. The soil rests on a 1-inch-thick layer of absorbent cotton. After most of the replaceable cations and other soluble matter have been extracted by the KCl, the solution comes through clear and nearly free of zinc. This arrangement provides plenty of KCl solution with little trouble. The soil used is a silty clay of pH 7.1.

*Potassium Bisulfate.*—Zinc-free potassium bisulfate,  $\text{K}_2\text{S}_2\text{O}_7$ , used in the estimation of total zinc, is not commercially available. To prepare a supply as free of zinc as is practical, obtain the purest available  $\text{K}_2\text{SO}_4$  and free it of zinc by a modified Steinberg (11) treatment; place 20 grams of the zinc-free  $\text{K}_2\text{SO}_4$  in a platinum dish, add 6 cc of concentrated  $\text{H}_2\text{SO}_4$ , heat below redness for a few minutes to avoid loss of much  $\text{SO}_3$ , and finally heat to quiet fusion for a few minutes. After the melt is cool, it is easily removed from the platinum dish and granulated for use by breaking up in a porcelain mortar. This preparation contains some zinc, so that it is necessary to keep account of the amount used in order to make proper correction for blank.

*Quartz Sand.*—Quartz sand, at least approximately free of easily soluble zinc, is needed for certain filtration techniques. To prepare it, digest white silica sand, containing over 99 per cent  $\text{SiO}_2$ , on the steam bath with dilute HCl (1+3) several hours, wash, and digest with acid repeatedly until the acid wash is not colored and contains only small amounts of zinc. Next, digest with 2 N zinc-free HCl. Then transfer to a Buchner filter, wash out the acid, rinse with dilute HF, and wash with pure water till free of acid. Dry and place in a clean glass bottle.

Thus prepared, the sand still contains some zinc that is extractable by 0.05 N HCl; therefore suitable blanks should be run with whatever solvent is being used, in order to make corrections for zinc from the sand.

*Amount of Zinc in the Blank.*—Sometimes the blank constitutes a



large part of the total zinc extracted so that the final result is of uncertain value; for the exact amount of the blank is not precisely known. Some of the extracts, such as those of soils 144 and 145 (table 3, p. 11), contain very little more zinc than the reagent solution itself.

## METHODS OF SEPARATING EXTRACTS FROM UNDISSOLVED MATTER

*Filtration.*—Much time and labor have been spent in seeking or devising a satisfactory filter for separating the insoluble part of the soil from the extracts. Chief requirements are that the filter should operate rapidly, remove undissolved solids from the solution completely, and not add to or remove zinc from the solution passing through it. No filter which satisfies all these conditions has been found: cheap filter paper adds zinc to the solution passing through it; expensive acid-washed filter paper is likely to retain tenaciously some of the zinc removed from the solution. These statements apply to both filter-paper sheets and filter-paper pulp. It was not found possible to wash even a new porcelain Buchner funnel free of zinc. All the usual sintered-glass filters, even if made from Pyrex, give up zinc to acid solvents. It was very difficult to wash white silica sand, over 99 per cent  $\text{SiO}_2$ , free of easily soluble zinc.

The paper-pulp-and-sand filter is fairly satisfactory and permits rapid filtration; it is made as follows: In a filter tube 35 mm in diameter, 12 cm long, is placed a perforated porcelain disk. This supports a pad of paper pulp, the actual filter. On top of the filter pad is a layer of washed zinc-free sand. The sand retains most of the soil sample, which is placed on top of the sand, so that only a little of the soil reaches the filter-paper pad. More sand is added above the soil. Above this sand is placed another perforated porcelain disk, which largely prevents disturbance of the sand when liquids are poured in. The filter tube is large enough to hold 50–75 cc of liquid above the upper porcelain plate. It is used for downward percolation of soils by any desired solvent. The rate of percolation is 25–100 cc or more per hour. Unless the solvent has a flocculating effect, the effluent from this filter is liable to be somewhat turbid when clay soils are being extracted. These paper-pulp-and-sand filters usually adsorb 1–5 gammas of zinc from the solution passing through them.

Finally, some well-washed Pyrex glass was crushed and sifted to about 100 mesh, then washed with hot  $\text{HCl}$ , with frequent changes during several days. This washed powder was made into sintered-glass filter disks, which after some washing with acid gave up no more zinc to dilute  $\text{HCl}$ . But after being washed free of zinc, they do absorb a little zinc from a

weak solution passing through them. They are preferable to paper filters because they are easier to operate automatically, and because it is easier to recover, by acid extraction, any zinc adsorbed by the filter, after the soil has been washed out of the filter. This filter was found unsatisfactory for use with dilute aqueous suspensions which contain very little electrolyte, because in absence of a flocculating agent it also required a mat of filter-paper pulp in order to secure a rapid enough rate of percolation as well as a clear filtrate when the solvent was 0.01 *N* HCl plus 40 p.p.m. calcium. But the filter operated very well when the solvent used to extract zinc was changed to 0.5 *N* KCl plus acetic acid (p. 17); this solvent prevented deflocculation of the soil and thus permitted a satisfactory rate of percolation.

*Upward Percolation.*—Downward percolation of a weak solvent, such as CO<sub>2</sub>-saturated water (p. 14), through a soil, tends to clog the filter so that percolation becomes very slow. Some of the dissolved zinc is fixed in the filtering medium. Furthermore, with CO<sub>2</sub>-saturated water, the CO<sub>2</sub> gas tends to separate from the water above the soil, replace the solution coming down through the supply siphon, and thus stop operation. These difficulties are almost completely avoided by causing the solvent to pass up through the filter, then through the soil, and out at the top of the filter tube to a suitable receiver.

The water for upward percolation is placed in a 2-liter flask into which a stream of CO<sub>2</sub> is continually passed (fig. 1). From this flask a siphon conveys the solution to a 300-cc flask, which supplies it to the percolator by means of another siphon, in which is a stopcock for regulating the flow to the percolator. Another stream of CO<sub>2</sub> enters the 300-cc flask continually in order to keep the solvent saturated with the gas. The percolator in which the soil is placed is shaped like a U-tube, the inlet side about 18 mm in diameter, the percolator side about 35 mm in diameter. This percolator tube is made from the neck of a broken 800-cc Kjeldahl flask, into which is fused a sintered-glass filter disk, on which the soil rests. The soil is mixed with five times its weight of quartz sand in order to favor action of the solvent on the soil. The narrower side of the U-tube is connected with the solvent-supplying siphon by means of a bored cork through which the siphon tube passes (fig. 1). The solvent comes down into the narrow side of the U-tube, up through the filter plate, and rises through the soil until it reaches the end of another siphon tube which passes through a two-hole cork in the top of the percolator tube. The second hole in the cork is closed by a glass tube with rubber tube and pinch clamp. The solvent rises through the soil and overflows through the siphon into a receiver for the extract, without coming in contact with



the cork in the top of the percolator. The emptying siphon may be slid up or down through the cork in the percolator in order to draw off more or less of the solution above the soil. The other tube, with rubber and pinch clamp, aids in drawing off the solution as desired, by blowing into it, much as a wash bottle is operated.

By means of the stopcock in the supply siphon, the solvent is regu-

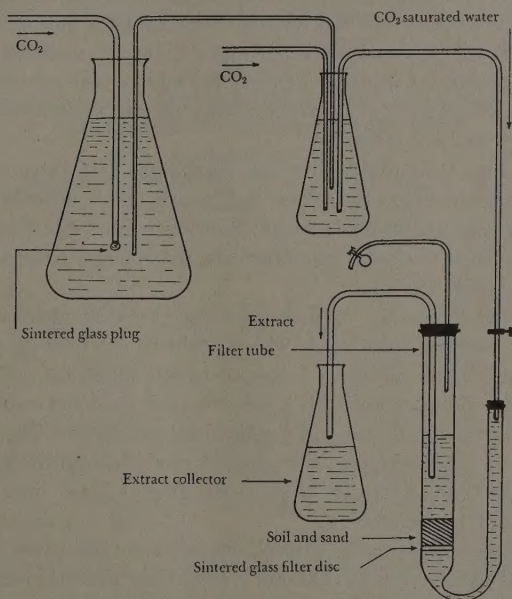


Fig. 1.—Apparatus for upward percolation with  $\text{CO}_2$ -saturated water.

lated to flow at a slowly dropping rate of 200 to 300 cc per hour, according to the quality of the soil being extracted. The flow should be slow enough so that very little soil is carried over. At first some soil goes into suspension and may be carried over, but after a time the solution becomes nearly clear. If not clear, it is allowed to stand overnight, when the clear solution may be decanted off for analysis.

After the percolate begins to come through clear, the rate of flow may be increased if desired, without causing much turbidity. The sandier the soil, the less likely is it to be carried over and produce turbidity. The main reason for operating the extraction by upward instead of downward percolation is that in this way the filter is not clogged by fine soil

so that percolation at the same rate may be continued indefinitely. Furthermore, zinc from the soil is not fixed in the filter.

All glassware used is Pyrex and the apparatus is so arranged that the soil and the solvent come in contact with nothing else, and thus there is no opportunity for the solvent to take up zinc from rubber connections or ordinary glass.

Frequent attention is necessary to maintain smooth operation of this apparatus: the reservoirs and siphons must be kept full of solution to avoid blocking the operation with  $\text{CO}_2$  gas which has escaped from solution, and a constant supply of  $\text{CO}_2$  gas for making the solution must be maintained. However, the apparatus may be run satisfactorily for an hour or more without attention.

*Centrifuging.*—Centrifuging for clarifying soil extracts was not found practicable unless the solvent had considerable flocculating effect, and under these conditions sedimentation overnight clears the solution without the use of the centrifuge. Besides, the volumes to be handled are too large for centrifuging.

*Equilibrium Extracts.*—In order to escape the difficulties with filters, equilibrium extracts were made which could be clarified by sedimentation. An equilibrium extract is defined as one made by agitation of a somewhat soluble material with a solvent until essential equilibrium is attained between the liquid and the undissolved matter. The procedure here described gives extracts only approximately in equilibrium with the soil, since the time of contact of soil with solvent is not long enough to produce complete equilibrium.

When extracts were made with water, sedimentation was unsatisfactory because these extracts required a long time to settle clear without filtering. This difficulty is avoided by use of a salt solution, 0.5 *N* KCl plus enough acetic acid to make the pH 3.2 and the titratable acidity 0.04 *N*; this solvent is discussed on page 17.

The procedure used in extracting the zinc is as follows: To a 500-cc Pyrex glass-stoppered cylindrical-shaped bottle add 400 cc of solvent, then 5 grams of soil. Insert the stopper and fasten by a rubber band placed over the top and tied to the neck. Lay the bottle on the "roller"<sup>7</sup> described by Furnstal (7) and rotate at about 35 r.p.m. for 4 hours. After the bottle has stood overnight to clarify, siphon off the clear liquid within 2–4 cc, add 400 cc solvent, and again rotate for 5 hours. Usually only two extracts of the same portions of soil are made. But the process may be repeated as many times as desired.

<sup>7</sup> The "roller" consists of two horizontal rubber-covered shafts rotated by a small motor through suitable speed-reducing gear.

This method provides a clear solution without the use of any filter and no special apparatus except the "roller."

Extraction of a solute from a soil by means of a weak solvent is a reversible reaction depending on relative concentrations in the two media. Accordingly, it is often necessary to employ large volumes of a solvent in relation to the amount of soil in order to carry extraction of a difficultly soluble minor constituent to near completion.

*Comparison of Percolation and Equilibrium Methods.*—Soil extracts

TABLE 3  
ZINC EXTRACTED FROM 2 GRAMS OF SOIL BY UPWARD PERCOLATION WITH  
CO<sub>2</sub>-SATURATED WATER OF pH 4, ACID 0.019 N  
(Each percolate 250 cc)

Soil	Zinc in percolate					Sum	Blank	In soil	
	1	2	3	4	5			2-gram sample	On basis of air-dry soil
	γ	γ	γ	γ	γ	γ	γ	γ	p.p.m.
30.....	1.0	0.8	0.6	0.6	—*	3.0	1.2	1.8	0.90
35.....	1.0	0.5	0.5	0.4	0.3	2.7	1.5	1.2	0.60
65.....	1.3	1.0	0.8	0.5	0.5	4.1	3.0	1.1	0.60
78.....	2.7	1.2	1.0	1.2	1.0	7.1	1.5	5.6	2.80
95.....	0.7	0.5	0.4	0.3	—	1.9	1.2	0.7	0.35
112.....	1.3	1.1	0.6	0.6	—	3.6	1.2	2.4	1.20
136A.....	4.5	3.5	2.0	1.7	1.0	12.7	1.5	11.2	5.60
136B.....	1.0	0.8	0.6	1.2	—	3.6	3.0	0.6	0.30
144.....	0.4	0.3	0.3	0.3	—	1.3	1.2	0.1	0.05
145.....	0.8	0.6	0.4	0.5	—	2.2	2.0	0.2	0.10

\* Dashes indicate data not available.

may be separated from the soil by use of ordinary paper filters or filter tubes, or by sedimentation. Paper filters are simple but slow, require much of the operator's time and attention, and may give turbid extracts and imperfect extraction. Filter tubes are faster in operation but require special care in preparation and considerable attention; they may be operated automatically. Both paper filters and filter tubes have the disadvantages of retaining some zinc and of imperfect extraction, unless the soil is mixed with much coarser material such as sand. Both have the advantage of separating the extract into aliquots which may be tested frequently (sometimes important) to determine how far toward completion the process has gone. They can quickly supply a clear solution for immediate testing. The rate at which zinc is extracted by percolation may indicate to some extent the ease of solution of soil zinc, or the rate at which it will be delivered to growing plants by the soil, which equilibrium extracts cannot do. The zinc in sandy soil 112 is extracted with



a much smaller volume of solvent than is the zinc in clayey soil 65 (table 3).

Equilibrium extracts need less apparatus, clear by sedimentation after some hours, are simple, but require much agitation. They are free from absorption by filter media, take little of the operator's time and attention to get clear extracts, but require repetition to complete the extraction. However, for routine work where mechanical agitation is available and the solvent used maintains flocculation, equilibrium extracts avoid the difficulties with filters and are most convenient.

### SOLVENTS FOR EXTRACTING AVAILABLE ZINC

Since only acid solvents extract much zinc from soils, and since soils have considerable buffer power, a suitable solvent for available soil zinc should evidently be somewhat acid and have some buffer effect so that its pH will not be greatly changed by reaction with the soil.

To give an indication of the zinc available to plants, the solvent, it is assumed, should not be much more acid than a possible soil solution, say pH 3.

Any solvent used for making equilibrium extracts should contain sufficient electrolyte to flocculate the clay so that the suspension will clear by sedimentation within a few hours.

Finally, the solvent should be one easily prepared free of zinc and convenient to use.

Many solvents in the course of this investigation were studied. Details of these experiments are omitted, but a number of the solvents are listed below, roughly in the order of increasing capacity to dissolve zinc from soils. Some of their characteristics are given, and those that most nearly meet the specifications just noted are discussed in more detail. Results with several of them are given in table 4, and tables giving results with some others are mentioned under the specific solvents. Besides those named below, some dilute alkalies and several other less satisfactory solvents were briefly studied.

*Water.*—Pure water has almost no solvent power for soil zinc (table 4, col. 7). A great difficulty with water percolation of soil is that part or all of the very small amount of zinc extracted from the soil becomes fixed in the filters (either paper or sintered glass) as the solution passes through, so that little or no zinc is found in the filtrate. This fixation is only partly avoided by using filters specially washed with HF. In consequence, it has not been possible to show positively that any of the zinc in natural soils is extractable with water alone. Soils to which much zinc has been added do give up some of it to pure water, though most of the

TABLE 4  
ZINC EXTRACTED FROM SOILS BY VARIOUS METHODS AND DIFFERENT SOLVENTS WITH OTHER DATA

Soil fertility and no.	pH of soil	Total zinc	Zinc in equilibrium extracts		Zinc in percolation extracts				Fixing power	Exchangeable zinc	Evidences of zinc deficiency*
			N HCl	0.005 N HCl	0.01 N HAc	CO <sub>2</sub> water		Water			
						p.p.m.	p.p.m.				
	1	g	g	p.p.m.	p.p.m.	p.p.m.	g	p.p.m.	g	p.p.m.	10
Fertile											
30.....	7.0	96	3	2	2	1.0	—†	—	0.14	None	
65.....	7.1	110	9	5	4	0.6	—	50	0.30	None	
103.....	5.9	123	10	2	3	0.4	0	50	—	None	
Medium fertile											
35.....	6.0	132	5	0.5	0.6	—	—	—	—	None	
78.....	5.3	82	6	5	10	2.6	0	0	1.40	—	
89.....	5.3	90	3	2	3	4.6	—	—	—	Little-leaf	
Sandy, poor											
112.....	7.8	112	9	0	1.7	1.0	—	10	0.10	Severe little-leaf	
125.....	7.7	170	6	0	0.8	0.5	—	11	—	Little-leaf	
129.....	7.4	55	4	0	0.6	0.9	—	—	—	Little-leaf	
136A.....	6.7	72	14	5	9.0	5.8	0	0	0.50	No white bud of corn	
136B.....	8.1	59	9	0.5	0.5	0.2	0	11	0.10	Little-leaf and white bud	
Alkaline											
80.....	8+	105	5	2	2	0.4	—	95	0.14	—	
95.....	8.3	70	13	2	4	0.6	—	30	—	Mottle-leaf of citrus	
144.....	7.1	335	16	0	0.3	0.05	—	95	—	—	
Corral											
121A.....	7.7	74	32	4	12	1.0	—	—	—	Little-leaf†	
121B.....	7.9	66	23	2	11	0.5	—	—	—	Little-leaf†	
127B.....	7.4	112	15	6	6	0.2	—	—	—	Little-leaf†	
145.....	6.9	—	—	—	0.4	0.3	—	18	—	Little-leaf	

\* That is, evidence in the field, with no zinc added.

† Dashes indicate data not available.

‡ These soils are often very productive of many annual crops but fruit trees on them are diseased.

added zinc remains fixed by the soil (see "Fixing Power of Soils for Zinc," p. 26).

A modified sort of percolation with water which gives an extract similar to the displaced solution obtained by the method of Burd and Martin (5) was performed as follows: 1 kilo of soil is moistened to about field capacity. After standing overnight, the moist soil is packed into a glass percolator, a thin layer at a time, and compacted by a wood block. Then

TABLE 5  
ZINC IN DISPLACED SOIL SOLUTION

Soil no.	Percolate		Zinc in percolate	Zinc extracted from soil	Time
	No.	Volume			
		cc	γ	p.p.m.	days
30.....	{ 1	100	4.0	0.013	4
	{ 2	100	1.5		
	{ 3	100	4.0		
	{ 4	100	2.5		
	{ 5	80	1.0		
89A.....	{ 1	110	11.6	0.021	4
	{ 2	100	5.1		
	{ 3	200	2.6		
	{ 4	200	1.6		
95.....	{ 1	100	0.0	0.000	3
	{ 2	50	0.2		
103.....	{ 1	100	4.0	0.007	6
	{ 2	80	1.7		
	{ 3	200	1.5		
145.....	{ 1	100	2.0	0.004	1.5
	{ 2	100	1.0		
	{ 3	100	1.0		

water is added on top and the percolate is collected without the use of pressure. From sandy soils the solution is obtained easily, from loams and clays with difficulty or not at all. In most cases, percolation is very slow and the amounts of zinc extracted are very small and decrease rapidly in successive percolates because the electrolytes have been largely removed from the soil. After the bulk of the easily soluble salts in the soil is extracted, little more zinc dissolves in the replacing water. The volumes of successive portions of the percolate from some of these soils were more than the volume of the soil solution contained in the soil at the beginning of percolation, in others they were less. Percolation from the sandy soils, for example, nos. 30 and 89, may continue indefinitely.

Probably the zinc thus extracted is dissolved in the soil solution. But from these observations and the figures given in table 5, it seems that the



zinc in the extract obtained in this manner should be considered as exchangeable rather than water-soluble; for, under these conditions the solution contains some salts dissolved from the soil, and cations of these salts replace zinc. (See also "Exchangeable Zinc," p. 24.)

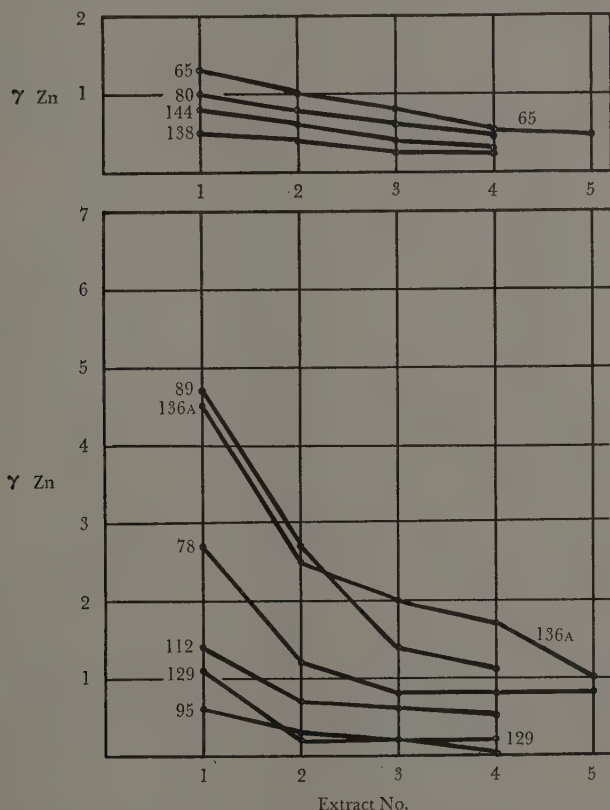


Fig. 2.—Zinc extracted by  $\text{CO}_2$ -saturated water by upward percolation; 2 grams of soil and 250 cc extract in each case. (Data from table 3 and laboratory records.)

*Weakly Alkaline and Neutral Salt Solutions.*—One per cent  $\text{K}_2\text{CO}_3$  and other weak alkaline solutions did not extract zinc.

Neutral salt solutions extract very little zinc (table 7, col. 1). Recently, a modified procedure using 5 grams of soils on a sintered-glass filter and extracting with neutral 0.5 N KCl has dissolved amounts of 0.00 to 0.14

p.p.m. of zinc from several soils. Soil 78, which frequently gives erratic results with other solvents, gave 1.8 p.p.m. of zinc by this method.

Normal  $\text{NH}_4\text{Cl}$  works well but was not used because it is more expensive than  $\text{KCl}$  and has no advantages over the latter.

*Water Saturated with Carbon Dioxide.*—A saturated solution of  $\text{CO}_2$  in water dissolves more or less zinc from nearly all soils (table 4, col. 6; table 6, col. 1). This is taken to indicate that in the vicinity of active roots, where  $\text{CO}_2$  is being set free, some zinc is present in the soil solution.

Figure 2 (p. 16) and table 3 (p. 11) are presented in order to give a clearer idea of the course of extraction with  $\text{CO}_2$ -saturated water, the magnitude of the amounts of zinc in successive percolates, the correction for blank, and the total amount of zinc extracted.

In many ways,  $\text{CO}_2$ -saturated water seems the most appropriate solvent, and was used on many soils; but it is very inconvenient.

*Solutions Saturated with Carbon Dioxide.*—Soil solutions commonly contain phosphate and silica; therefore it seemed of interest to determine the influence of phosphate and soluble silica on the amount of zinc extracted by  $\text{CO}_2$ -saturated water. Some results are shown in table 6. The phosphate, which was added at the rate of 10 p.p.m. to the water as a neutral mixture of  $\text{NaH}_2\text{PO}_4$  and  $\text{Na}_2\text{HPO}_4$ , tends to depress solubility of zinc in  $\text{CO}_2$  extracts.

The silica was added as water-glass, which had been made very dilute and nearly neutral, at the rate of 5 p.p.m.  $\text{SiO}_2$ . This also seems, in some cases, to depress solubility of zinc in  $\text{CO}_2$ -saturated water. Very great increase of the amount of silica in solution tends to interfere with extraction of zinc from the solution by dithizone.

Figures in table 6 permit a comparison of the amounts of zinc extracted by four different solvents saturated with  $\text{CO}_2$ . The 0.5  $N$   $\text{KCl}$  with  $\text{CO}_2$  extracts much more zinc than  $\text{CO}_2$ -saturated water alone. But there appears to be no advantage in the use of this solvent instead of the  $\text{KCl}$  with acetic acid, described below. It is much less convenient than the latter.

*Acetic Acid.*—Acetic acid is more comparable to  $\text{CO}_2$ -saturated water than are mineral acids and more convenient to use than  $\text{CO}_2$ ; furthermore, it is easily prepared and well-buffered. It is not effective at 0.001  $N$  strength. Many tests were made with 0.01  $N$  acetic acid, and seemingly good results were obtained (table 4, col. 5). It is very cumbersome to use, however, because of the large volume of the dilute acid required (1,500 to 2,000 cc to extract the easily soluble zinc from 2 grams of soil). A concentration of 0.04  $N$  was more effective (table 8, col. 1) and prevented much fixation of zinc in the filter media. But while acetic acid of

this strength is a good solvent for easily soluble soil zinc, it has insufficient flocculating effect for use with equilibrium extracts.

*Calcium Chloride plus Acetic Acid.*— $\text{CaCl}_2$  plus acetic acid is not a good solvent; for if it is strong enough to be effective, the solution con-

TABLE 6  
ZINC\* BY UPWARD PERCOLATION OF SOILS WITH WATER+ $\text{CO}_2$  AND  
OTHER SOLUTES

Soil no.	$\text{CO}_2$ water	$\text{CO}_2+\text{PO}_4$ water	$\text{CO}_2+\text{SiO}_2$ water	0.5 N $\text{KCl}+\text{CO}_2$
	1	2	3	4
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
30.....	1.0	—†	—	1.3
35.....	0.6	—	—	3.0
59.....	0.6	—	—	8.5
64.....	0.7	1.0	0.2	2.7
65.....	0.6	—	—	2.2
78.....	2.6	1.5	1.7	3.7
80.....	0.4	—	—	2.0
86.....	0.3	—	—	2.2
89.....	4.6	—	—	5.6
95.....	0.6	—	—	3.0
103.....	0.4	0.3	0.5	2.3
112.....	1.0	0.5	0.2	1.5
121A.....	1.0	—	—	5.4
121B.....	0.5	—	—	4.8
122.....	0.6	0.3	0.2	0.6
125.....	0.5	—	—	1.0
127B.....	0.2	—	—	1.2
129.....	0.9	—	—	0.9
136A.....	5.8	4.6	6.0	5.8
136B.....	0.2	0.3	0.1	0.6
137.....	0.6	—	—	1.3
138.....	0.5	—	—	1.1
144.....	0.05	0.0	0.0	0.4
145.....	0.1	—	—	0.4

\* In this table "zinc" includes small amounts of Cu, Co and Pb extracted by the solvents, but not separated from the zinc.

† Dashes indicate data not available.

tains too much  $\text{Ca}^+$ , which interferes in the determination of zinc by dithizone.

*Acetate Salts plus Acetic Acid.*—Sodium acetate and ammonium acetate plus free acetic acid make good active solvents (table 7, cols. 2 and 3) but are not easily obtained free of zinc. Furthermore, since they have very high buffer power, much ammonia is required to neutralize the extracts made with them for determination of zinc. Usually such extracts require a high blank correction.

*Potassium Chloride plus Acetic Acid.*— $\text{KCl}$  plus acetic acid proved the most satisfactory solvent tried. It dissolves about the same amounts



of zinc as 0.4 *N* acetic acid (compare cols. 1 and 2 of table 8) but has an advantage over the latter because, as previously mentioned, its flocculating effect is adequate for equilibrium extracts. KCl is cheap, easily prepared free of zinc by the method described on page 6, and convenient to use.

It was used at concentrations of 0.5 *N* and *N* KCl; the former is nearly as effective as the latter. Enough free acetic acid is added to make the

TABLE 7  
ZINC EXTRACTED BY NORMAL AMMONIUM ACETATE AT THREE  
DIFFERENT pH LEVELS

Soil no.	Zinc in soil at:			Exchange capacity
	pH 7.2	pH 6.5	pH 5.6	
	1	2	3	4
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>m.e. per 100 grams</i>
30.....	0	0.4	1.3	4.9
59.....	6	11	25	17.4
65.....	0	2.0	1.7	17.4
78.....	3	11	11	5.5
95.....	0	0.7	4.0	6.2
122.....	0	0.3	2.5	4.9
136A.....	3	4	6	2 <sup>+</sup>
144.....	0	0.5	0.5	25 <sup>+</sup>
145.....	0	0	1.5	2 <sup>+</sup>

pH 3.2 and the titratable acidity 0.4 *N* with bromothymol blue indicator, by actual test of each lot prepared; about 2.5 cc of glacial acetic acid per liter is required.

Results with 0.5 KCl plus acetic acid under various conditions are shown in columns 2 to 7 of table 8 and in table 9. This solvent has good replacing power, due to both K<sup>+</sup> and H<sup>+</sup>; whether the zinc extracted from soil by an acidified salt solution is dissolved by the replacing effect of the cation of the salt or by the similar replacing effect of the H<sup>+</sup> of the acid is an open question; see "Exchangeable Zinc," page 24.

*Citric and Tartaric Acids.*—Citric and tartaric acids are much more effective solvents than acetic acid, so that they tend to bring into solution troublesome amounts of iron, aluminum, manganese, and calcium; besides, the preparations obtainable contain some zinc, from which they are not easily separated.

*Inorganic Acids.*—Dilute HCl or H<sub>2</sub>SO<sub>4</sub>, even of 0.01 *N* strength, attacks soil too strongly and is a much more active solvent than are ordinary soil solutions; besides, it dissolves too much iron, which is objectionable with the dithizone method for estimating zinc.

Strong HCl can extract nearly all the zinc in soils except that contained in the resistant silicates. Most of the zinc dissolved by only strong acids is probably unavailable to plants. The use of *N* HCl for a rough estimate of total zinc is described on page 22.

*Effect of pH.*—The effect of increased activity of solvents is shown in

TABLE 8

EFFECT OF METHOD OF EXTRACTION AND OF VARYING RATIOS OF SOIL TO SOLVENT ON AMOUNT OF ZINC EXTRACTED BY 400 CC OF SOLVENT

Soil no.	Zinc in equilibrium extracts with						Zinc in percolation extract with 0.04 N acetic acid in 0.5 KCl, 5 grams soil
	0.04 N acetic acid, 1 gram soil	0.04 N acetic acid in 0.5 N KCl					
		1 gram soil	2 grams soil	5 grams soil	10 grams soil	200 grams soil	
		1	2	3	4	5	
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
30.....	7.4	7.6	5.4	3.4	1.9	0.47	3.9
64.....	5.0	4.8	5.0	4.1	—*	0.51	3.1
65.....	6.9	6.8	5.6	3.9	1.8	—	3.3
78.....	9.1	4.8	5.6	3.7	5.9	2.40	5.7
103.....	5.5	4.8	4.8	3.4	3.3	—	3.6
112.....	5.6	4.1	3.5	2.4	—	—	2.3
125.....	5.1	2.4	3.4	1.9	1.1	—	1.4
144.....	4.3	3.1	2.7	1.8	0.5	—	1.1

\* Dashes indicate data not available.

tables 4 (p. 13) and 7 (p. 18) and in section C of table 9. In general, the more acid the solvent the more zinc it will dissolve from the soil. Numerous other experiments, not here reported, with solvents of varying acidity, indicate that with sandy soils, such as nos. 30 and 78, some variation in acidity makes little difference, but with clay soils, such as no. 103, solvents of greater acidity extract more zinc.

*Influence of the Ratio of Solvent to Soil.*—In the beginning of the study, attempts were made to extract available zinc from soils with a small proportion of water, or other weak solvent, to soil. Little zinc was obtained, and much of that little was held in the filter.

The difficulties were so great and the results so unreliable that a radical change in procedure was made. The ratio of soil to solvent was changed from 1:1 or 1:5 to 1:100 or 1:200.<sup>8</sup> Fairly consistent replicate results were secured with the latter ratios, when the paper-pulp-and-sand filter described on page 7 was used. Many other results were as consistent as those given in part D of table 9, or more so, but some were

<sup>8</sup> Other changes in procedure, made to avoid the difficulties with filters, are discussed on pp. 20 to 21.

less so. Variations of 10 per cent of the amounts found were frequent in replicate tests made at different times. Replicate tests made at the same time agreed much better.

Some results of varying the ratio between 1:100 and 1:400 are shown in section B of table 9. As shown in section B, change of the ratio from 1:150 to 1:250 makes little difference. With some soils, considerably greater changes in the ratio make little difference; with others, results are materially affected. Since the process is arbitrary, the ratio 5 grams of soil to 400 cc of solvent has been selected for convenience in extractions with KCl and acetic acid solvent. Some other ratio might do as well. This one was adopted after consideration of the results of the experiments indicated in table 9, section B.

TABLE 9

EFFECT OF VARIATION OF CONDITIONS ON AMOUNT OF ZINC FOUND IN EQUILIBRIUM EXTRACTS MADE WITH 0.5 N KCl SOLVENT

(2 grams of soil and 400 cc 0.5 N KCl solvent except where otherwise indicated; stirred by rotating 500-cc bottles on "roller")

A. TIME VARIED					
Soil no.	Time	Zinc	Soil no.	Time	Zinc
	<i>min.</i>	<i>p.p.m.</i>		<i>min.</i>	<i>p.p.m.</i>
65.....	5	7.5	78.....	5	5.9
	30	8.9		30	5.6
	300	10.0		300	6.1

B. RATIO OF WEIGHT OF SOIL TO VOLUME OF SOLVENT VARIED					
Soil no.	Zinc extracted with a ratio of soil to solvent of:				
	1:400 (1 gram to 400 cc)	1:250 (2 grams to 500 cc)	1:200 (2 grams to 400 cc)	1:150 (2 grams to 300 cc)	1:100 (4 grams to 400 cc)
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
65.....	13.4	—	10.0	—	—
78.....	8.6	10.3	5.5	11.0	5.2
103.....	—	10.9	—	10.5	—
112.....	—	3.5	—	3.2	—

C. ACIDITY OF SOLVENT VARIED				
Soil no.	Zinc extracted with			
	0.02 N acid	0.028 N acid	0.035 N acid	0.043 N acid
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
30.....	5.8	5.6	5.6	5.6
64.....	5.7	9.1	9.1	9.3
78.....	7.0	7.0	7.4	8.5
103.....	7.7	9.8	11.0	11.2



TABLE 9—(Concluded)

## D. REPRODUCIBILITY OF RESULTS

(All conditions of tests essentially alike in both tests)

Soil no.	Zinc extracted	
	May 2-4	May 4-6
	<i>p p.m.</i>	<i>p.p.m.</i>
30.....	6.3	7.0
78.....	9.5	8.8
122.....	6.4	5.3
144.....	3.8	4.2

## E. RECOVERY OF ZINC ADDED TO SOILS, WITH ZINC ADDED TO DRY SOIL BEFORE ADDING SOLVENT; 10 GAMMAS ADDED TO 2 GRAMS OF SOIL

Soil no.	Zinc originally present in soil	Zinc found after adding 10 gammas	Zinc fixed by soil
	$\gamma$	$\gamma$	$\gamma$
78.....	19	19.6	9.4
112.....	8	15.2	2.8
144.....	8	15.4	2.6

## F. RECOVERY OF ZINC ADDED TO SOILS WITH ZINC ADDED TO SOLVENT BEFORE ADDING SOIL; 10 GAMMAS ADDED TO 2 GRAMS OF SOIL

Soil no.	Zinc originally present in soil	Zinc found after adding 10 gammas	Zinc fixed by soil
	$\gamma$	$\gamma$	$\gamma$
78.....	19	23.2	6.8
112.....	8	18.0	0.0
144.....	8	16.0	2.0

Some equilibrium extracts have been made with the KCl solvent using a ratio of 1:2, that is, 200 grams of soil to 400 cc of solvent (table 8, p. 19). Although only a fraction of the easily soluble zinc is extracted by this treatment, the amounts of zinc thus obtained from different soils differ more widely than when a much larger proportion of solvent is used. This suggests that the procedure is better adapted to differentiating soils as to easily soluble zinc than the procedure in which a larger proportion of solvent to soil is used, although the latter extracts much more zinc. One advantage in using a greater proportion of soil to solvent is that the proportion of the zinc in the blank test to that from the soil is much less, which tends toward more reliable results. Numerous other results of variations of ratios of soil to solvent in equilibrium extracts are presented in table 8.

## ESTIMATION OF TOTAL ZINC IN SOIL

*Complete Decomposition.*—For accurate estimates of total zinc in the soil, complete decomposition is necessary. The procedure is as follows: Ignite 1 gram of the soil, 100 mesh, in a platinum crucible to remove moisture and organic matter, then add 5 grams of fused  $K_2S_2O_7$ , and adjust the heat to keep the mixture melted without causing loss of much  $SO_3$ . After 5–10 minutes, the heat is increased to low redness for a few minutes. Next grasp the crucible with the tongs, remove from the heat, and continually turn about in order to distribute the melt in a thin layer until it solidifies. When cold, add water and dilute HCl, and heat to dissolve the melt. Filter into a 100-cc flask and wash the insoluble sand, etc., until nearly free of salts. This is essentially the procedure of Boggs and Alben (4). Next burn the filter with contents, add HF, and evaporate dry on the steam bath. (The higher temperature of the hot plate might volatilize zinc.) Dissolve the residue in water with 2 or 3 cc of *N* HCl and filter into the flask containing the main solution. Sometimes there is an appreciable residue after the HF treatment. This may be decomposed by repetition of the above-described treatment. The residue from the first fusion often contains a considerable part of the total zinc. (Boggs and Alben did not carry out this decomposition with HF.) Zinc is determined in the acid solution by the dithizone method. The results obtained by this procedure are reported in column 2 of table 4 (p. 13).

*Zinc Dissolved by Normal Hydrochloric Acid.*—If the treatment is sufficiently drastic, a large part of the zinc in most soils will be brought into solution by strong acid. However, as knowledge of the amount of zinc thus dissolved seems unlikely to have much value for plant nutrition, the results are not reported. Instead, a simple procedure easily executed was adopted in making rough estimates of the amount of zinc in the soil. Five grams of the soil in a small flask is covered with 10 cc of *N* HCl and left 24 hours with occasional agitation. Then 90 cc of water is added and mixed. After standing overnight to settle, the clear solution is decanted off and suitable aliquots are analyzed for zinc. The amount found in this way is not known to be significant as a plant nutrient; it simply shows, with a minimum of effort, whether there is much or little zinc in the soil.

## EFFECT OF REMOVAL OF ORGANIC MATTER

May it not be possible that microorganisms in a soil which has little available zinc, absorb so much of what is available that higher plants

such as trees suffer for lack of zinc? Ark (2) has presented evidence suggesting that this actually occurred when corn and peach seedlings were grown in some soils of low zinc-supplying power. Removal of organic matter by ignition made it possible to extract more zinc from most fine-textured soils, but less from most sandy soils, by means of equilibrium extracts with 0.02 *N* HCl. The results could not be interpreted usefully.

In the present experiments, organic matter was removed by warm digestion with zinc-free  $\text{H}_2\text{O}_2$  in neutral solutions. Oxidation of organic

TABLE 10

EFFECT OF OXIDATION OF SOILS WITH  $\text{H}_2\text{O}_2$  ON COPPER, COBALT, AND ZINC EXTRACTED BY *N* KCl SOLVENT, pH 3.6

Soil no.	Zinc		Copper		Cobalt	
	Untreated soil	Oxidized soil	Untreated soil	Oxidized soil	Untreated soil	Oxidized soil
	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
64.....	4.5	4.0	1.4	3.7	4.5	4.2
78.....	4.5	4.0	1.5	1.5	1.4	2.3
112.....	1.2	1.6	0.0	0.0	0.4	0.2
122.....	2.2	1.6	0.5	0.0	0.4	0.4
136A.....	6.6	6.8	0.7	0.1	2.0	1.1
136B.....	1.4	1.6	0.0	0.0	0.2	0.9
144.....	1.3	1.6	0.0	0.0	0.4	0.9

matter by  $\text{KMnO}_4$  or by bromine in alkaline solution failed to increase the solubility of the zinc.

The results obtained on several soils before and after oxidation of organic matter, are presented in table 10. Differences in amounts of zinc found before and after oxidation are mostly within the probable error of analysis, apparently without significance.

### THE STATUS OF ZINC IN THE SOIL

*Solubility of Ores of Zinc.*—It was thought that a study of some of the common ores of zinc would indicate to some extent whether or not they might be found in ordinary soils. Samples of four zinc minerals\* were ground to pass a 100-mesh sieve and tested for solubility in various solvents. These ores are:

1. Franklinite, oxide, 42 per cent zinc, from New Jersey
2. Calamine, silicate, 54 per cent zinc, from Joplin, Missouri
3. Sphalerite, sulfide, 59 per cent zinc, from Joplin, Missouri
4. Smithsonite, carbonate, 2 per cent zinc, from Joplin, Missouri

By shaking with 0.02 *N* HCl, without heating, all of them were al-

\* Obtained through the kindness of Professor A. Pabst of the Department of Geology of the University of California.

most completely decomposed and the zinc dissolved. The samples of sulfide and of carbonate were less easily dissolved than were the oxide and silicate. All these ores were almost completely decomposed by 0.01 *N* acetic acid. Water saturated with  $\text{CO}_2$  also dissolved away most of the zinc from nos. 2 and 4, but left 14 per cent of the total originally present in nos. 1 and 3. All were largely decomposed and the zinc dissolved out by zinc-free distilled water.

Since soils easily fix zinc in water-soluble state, from which it is released by weak acids, as would be true of extraction of zinc from organic and inorganic colloids, these zinc minerals probably do not exist as such in ordinary soils. Most of the zinc in ordinary soils is probably held there by surface adsorption on the colloidal particles instead of in true chemical combination. Since, however, part of the zinc in the silicious portion of the soil is not extracted without decomposition of the silicates, this portion of the total zinc may exist in true chemical combination in the soil silicates and is unlikely to become available to plants until the resistant silicates are decomposed by weathering.

*Exchangeable Zinc.*—It is usually assumed that the zinc cation in soils is exchangeable as is exchangeable calcium or potassium. If much zinc is present, that is undoubtedly true. But whether the very small amount of easily soluble zinc present in most soils is subject to replacement by the cation of neutral salt solutions is questionable. In attempting to replace soil zinc by neutral *N*  $\text{NH}_4\text{Cl}$ , the same difficulty was met as in making water extracts. If the solution is made neutral, the very slight amount of zinc dissolved is fixed by the filter paper so that the filtrate contains no zinc; but when the soil was washed off the filter and the filter was extracted with dilute acid, a little zinc was dissolved, which shows that there had been some exchange followed by fixation of the dissolved zinc in the filter. In studies on the fixing power of soils, a neutral 0.002 *N* solution of  $\text{CaCl}_2$  did not extract zinc from most soils, but when a little zinc had been added to the soil and the mixture dried, the  $\text{CaCl}_2$  solution did extract a portion of the added zinc. It was necessary to add considerable zinc to fine-textured soils before any could be extracted by this  $\text{CaCl}_2$  solution even though the soils having no added zinc contained some zinc easily dissolved out by dilute acid.

The replaceable zinc reported by others, for example, Jones, Gall, and Barnette (10) was probably replaced by  $\text{H}^+$  instead of by the chief cations of the salts used. Indeed, these workers say that more zinc was extracted by  $\text{NH}_4\text{Cl}$  than by ammonium acetate, the result being "attributed to its lower pH." They present evidence that  $\text{ZnSO}_4$  is carried down through the soil by rain water. In the light of the present work,



this seems probable, because of the acid character of the soil they used and because of the replacing effect of other cations in the acid soil solution, and perhaps locally high concentrations of zinc.

Weakly acid solutions of salts, however, extract zinc from all soils examined. Whether this is partly due to replacement by the cation of the salt or entirely due to the increased concentration of hydrogen ion is uncertain. In all soils examined by the writer, except soil 78, it has been found that, as stated on page 19, the more acid the solvent, the greater is the amount of the zinc extracted; and that unless the solvent is somewhat acid, the small amount of zinc extracted is almost within the limits of error of the method of analysis. (See results in tables 4 and 7, pp. 13 and 18.)

Some workers have suggested that part of the zinc in most soils exists on or in the tetrahedra or octahedra of the alumino-silicates in such condition that large cations like those of calcium or potassium cannot enter to replace it, but the small  $H^+$  can do so.

*Distribution of Zinc among the Different-sized Particles of Soil.*—Since in general there is more easily soluble zinc in fine- than in coarse-textured soils, it is of interest to determine the amount of zinc in or on the clay, silt, and sand of various soils.

For this purpose, each soil was separated into three fractions according to particle size, by sedimentation in fifty to one hundred times as much water. *Sand* is arbitrarily defined as that fraction which settles through a depth of 15 cm in 15 minutes, *silt* as that which does not settle through 15 cm in 15 minutes but does settle through a depth of 30 cm in 24 hours, and *clay* as that which does not settle through that depth in that time. After the silt and sand had settled, the main part of the water remaining was removed by decantation and the rest by evaporation on the steam bath. The clay was separated from the water suspension by withdrawing most of the water by suction through a Pasteur filter candle and evaporation of the remaining water on the steam bath.

This somewhat tedious method of separating the fractions of the soil was used in order to avoid bringing the materials in contact with any medium which might absorb or remove zinc from the soil suspension. Some zinc, however, was adsorbed by the soils from the ordinary distilled water used for sedimentation so that the zinc content of the separates was materially increased. The results are given in table 11.

Besides the separation of soils into different sizes by sedimentation in water, a few soils, mostly coarse, were separated into four sizes by means of sieves of 20, 40, and 100 meshes to the inch. The parts per million of zinc and the percentage of the available zinc in the soil present in each

fraction are recorded in table 12. In every case, the finer the particles the greater is the amount of zinc extracted from the fraction of soil examined. In this table, the figures for zinc include some copper and cobalt.

The figures in tables 11 and 12 show that the greater part of the zinc in soils is in the finer particles, but that one cannot assume that the amount of zinc in a soil is proportional to the clay content.

*Fixing Power of Soils for Zinc.*—As has been commonly observed, if a solution of zinc is added to soil, some or all of the zinc is fixed by the soil

TABLE 11

AVAILABLE ZINC IN AND FIXING POWER OF DIFFERENT-SIZED PARTICLES SEPARATED BY SEDIMENTATION

Soil no.	Particle size	Per cent of soil	Available zinc	Fixing power of particles for zinc
		<i>per cent</i>	<i>p.p.m.</i>	<i>p.p.m.</i>
78.....	{ Clay.....	3	23.0	0
	{ Silt.....	10	12.0	2
	{ Sand.....	83	5.0	0
103.....	{ Clay.....	18	23.0	50
	{ Silt.....	17	15.0	30
	{ Sand.....	42	7.0	24
144.....	{ Clay.....	26	8.0	210
	{ Silt.....	12	1.4	35
	{ Sand.....	55	3.0	6
145.....	{ Clay.....	4	92.0	65
	{ Silt.....	6	22.0	4
	{ Sand.....	87	4.0	0

so that it is not extractable by water. In order to determine how much zinc must be added to a soil so that water may dissolve appreciable amounts from it, 2 grams of the soil were placed in 2½-inch porcelain dishes, 3–4 cc of water was added, then different amounts of a neutral solution of zinc as  $\text{ZnCl}_2$  were added and the whole dried in an oven at 38–40° C. When dry, the soil was washed into a wide-mouthed flask with 200 cc of water containing 0.008 gram of calcium as  $\text{CaCl}_2$  (equal to 40 p.p.m. calcium in the solution). The flasks were shaken frequently for several hours, then let stand overnight, and the clear extract decanted off and tested for zinc.

The fixing power of the soil is defined as the parts per million of zinc that must be added so that a 1:100 water extract will contain 1 p.p.m. zinc.

Water alone did not extract zinc unless great amounts of zinc had been added. But when a little calcium was added to the water, some of the added zinc was dissolved out. This concentration of calcium, 40

p.p.m., was not enough to replace zinc from the soils to which none had been added. It seems probable that when zinc is added to field soils, there is a sufficient concentration of electrolytes in the soil solution so that when percolation from rain or from irrigation occurs, some of the added zinc is replaced by other cations and carried to lower depths in the soil; see Barnette, *et al.* (3).

Some figures indicating the fixing power of soils for zinc are given in column 8 of table 4 (p. 13). Another example of fixing power is the fol-

TABLE 12  
ZINC IN DIFFERENT SIZE PARTICLES OF SOILS SEPARATED BY 20-, 40-, AND  
100-MESH SIEVES

Soil no.	Particle size	Proportion in soil	Available zinc	Soil no.	Particle size	Proportion in soil	Available zinc
		<i>per cent</i>	<i>p.p.m.</i>			<i>per cent</i>	<i>p.p.m.</i>
64	On 20.....	0	0.0	125	On 20.....	0	0.0
	On 40.....	0	0.0		On 40.....	30	0.8
	On 100.....	50	4.1		On 100.....	40	0.8
	Through 100.....	50	6.1		Through 100.....	30	2.0
95	On 20.....	0	0.0	129	On 20.....	10	1.4
	On 40.....	70	2.0		On 40.....	50	1.4
	On 100.....	15	4.4		On 100.....	30	2.0
	Through 100.....	15	4.4		Through 100.....	10	6.8
112	On 20.....	0	0.0	136A	On 20.....	0	0.0
	On 40.....	20	1.1		On 40.....	22	3.4
	On 100.....	40	1.1		On 100.....	63	5.2
	Through 100.....	40	2.9		Through 100.....	15	7.6

lowing: To 5 grams of soil on a sintered-glass filter, acidified KCl solvent was added until but little more zinc was extracted. Then the KCl was washed out with water and the filter drained. Next, small amounts of  $ZnCl_2$  in water were added, the soil drained and washed out with water, and the solution tested for zinc. This process was repeated until a material increase of zinc appeared in the percolate. This required 22 gammas of zinc for soil 136 B, and more than 44 gammas of zinc for soil 65. This added zinc was not washed out by water, but was quickly removed by acidified KCl solvent.

### SUMMARY

Proper purification of apparatus and chemicals is very important in the determination of zinc content of soils.

The highly sensitive dithizone method is used for determination of zinc because of the very small amounts of zinc usually found in soils and the convenience of the method.

Considerable difficulties were experienced with filters used to sep-

arate extracts from soils; the fairly satisfactory sintered-glass-with-sand filters finally devised are described.

Of the numerous solvents used for extracting zinc from soils, the two finally selected are a saturated water solution of  $\text{CO}_2$  and 0.5 *N* KCl plus some acetic acid. Only acids extract much zinc from soils. Weak acids are used because they are somewhat similar in solvent power to the ordinary soil solution. The greater the acidity of the solvent, the more zinc will it extract from soil; very little is extracted unless the pH is below 7.

Methods for extracting the total zinc and various fractions of it by solvents of different power have been studied.

Both percolation and equilibrium methods have been used for making soil extracts. Extracting by upward percolation avoids the resorption of zinc after it has been extracted by the solvent, such as occurs with downward percolation because of absorption and adsorption of zinc in or on filter media.

Equilibrium extracts are convenient for routine work because they are simple and no kind of filter is needed.

The results of removal of organic matter from soils by burning and by action of  $\text{H}_2\text{O}_2$  failed to show any considerable difference in the solubility of the soil zinc before and after these treatments.

Four different ores of zinc were studied and found to be almost completely soluble in very dilute acids. Probably, therefore, these zinc minerals do not exist as such in ordinary soils.

A study of the distribution of zinc on different sized particles of soils shows that there is a considerably greater concentration on the smaller than on the larger particles so that clay soils are usually better supplied with zinc than sandy soils.

A procedure for measuring the power of soil to fix zinc in a water-insoluble condition is described. Probably much, if not all, of the easily soluble zinc in ordinary soils exists there mostly on the surfaces of particles either mineral or organic or both, held by surface attraction, instead of in true chemical combination. This view is supported by the following: small amounts of zinc are almost everywhere present in soils; zinc is easily fixed in the water-insoluble state on mineral and on organic substances; zinc ores are easily decomposed by water; soil zinc is not easily replaced by the cations of neutral salt solutions.

The original purpose of this study, to devise a method of determining by laboratory test whether additional zinc is needed to produce healthy plants on a given soil, has been only partially accomplished. In a large number of cases, actual trial with plants will be necessary to give a positive answer. This is also true with respect to other plant nutrients.



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